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On Malonic Nitrile

and Some of its Derivatives

INAUGURAL DISSERTATION

SUBMITTED TO THE UNIVERSITY OF CHICAGO FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

—BY—

BERNHARD CONRAD HESSE

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On Malonic Nitrile and Some of Its Derivatives.

Malonic nitrile, prepared in 1886 by L. Henry,[1] was studied by him to but a slight extent. He showed that on distillation it did not polymerize; that with cold concentrated hydrochloric acid malonic acid was readily formed; whereas in sealed tubes at 150°, it was split into chloracetic acid and carbon dioxide. With ammoniacal silver nitrate he obtained a salt which contained an amount of silver approaching that required by the formula $C_3Ag_2N_2$. So far as has been recorded syntheses by means of the salts of malonic nitrile have not been made.

The work to be described in the following pages was carried out under the supervision of Professor Nef of this university. Its object is to study some of the derivatives of malonic nitrile and to ascertain, if possible, whether in its salts the metal is bound to nitrogen or to carbon. Judging from the work on acetoacetic ester and its congeners as well as that on malonic ester, the 1.3 diketones and the nitroparaffins, it seemed quite unlikely that the metal is bound to carbon. That it is bound to nitrogen appears very probable because of the work on prussic acid and the cyanides.[2]

Cyanacetamide.

Preparation.— Cyanacetamide was prepared according to Van't Hoff's method[3] from cyanacetic ester and aqueous ammonia. The best yield as well as the purest product is obtained by slowly pouring cyanacetic ester (one molecule) into two molecules of 28-per cent. ammonia water, both reagents being at 0°. The ester dissolves and the amide soon separates out as a closely felted mass of crystals; the mass is now cooled to —15° and transferred to a Hirsch funnel, washed with ice-water until the odor of ammonia is only slight, spread on clay

[1] Compt. Rend., **102**, 1394. [2] Nef, (1895): Ann. Chem. (Liebig), **287**, 265-359.
[3] Van't Hoff, (1874): Ber. d. chem. Ges., **7**, 1382.

plates, dried in the air and finally at 100°. The yield varies from 70 to 75 per cent. of the theory.

Properties.—Thus prepared, cyanacetamide is a white substance crystallizing in hexagonal plates, melting without decomposition at 120°. It cannot be distilled either at ordinary or at reduced pressure without decomposition. It is soluble in 6.5 parts of cold water, 55 parts of cold alcohol, and is not very soluble in ether, chloroform or ligroïn. It dissolves in caustic soda solution with slow evolution of ammonia.

The fact that cyanacetamide is less soluble in alcohol than in water suggested that alcoholic ammonia would give a better yield. This is not the case, since with two molecules of a 16-per cent. alcoholic ammonia only 28 per cent. of the theoretical yield of the amide was formed, while with one molecule of alcoholic ammonia no separation whatever took place.

The clear solution of the ester in the aqueous ammonia followed by precipitation of amide has suggested the existence of an intermediate unstable addition-product which by loss of alcohol yields amide. This view has apparent support, at least, in the fact that the yield with alcoholic ammonia is only one-third of that obtained in the aqueous solution, although the solubility in water is very nearly ten times greater than in alcohol. The reason for this may be that in alcoholic solutions loss of alcohol by this addition-product with subsequent formation and precipitation of amide is prevented by the surrounding alcohol, a condition of things not found in the aqueous solution.

Sodium Cyanacetamide.—Dry cyanacetamide suspended in dry and alcohol-free ether is not attacked by sodium. On adding a few drops of alcohol reaction sets in at once, a light yellow salt being formed. It is necessary to add a few drops of alcohol from time to time. The reaction being completed the salt is removed from the ether and dried over paraffin *in vacuo*.

On analysis 0.4199 gram substance gave 0.2911 gram Na_2SO_4.

	Calculated for $C_3N_2H_3NaO$.	Found.
Na	21.70	22.48

Two atoms of sodium cannot be taken up.

The monosodium salt in chloroform suspension readily reacts with bromine, but the reaction-products were not further investigated.

Dibromcyanacetamide, $Br_2C\begin{smallmatrix}CN\\ C\\ NH_2\end{smallmatrix}O$.

Cyanacetamide in cold aqueous solution, treated with one molecule of bromine reacts at once. An oil separates, which after standing, becomes crystalline when scratched. Hydrobromic acid and ammonium bromide are also formed. The crystalline body thus obtained is not, as would be expected, monobromcyanacetamide,[1] but is the dibrom derivative. It is formed to the extent of 50 to 60 per cent. of the theory. After recrystallizing from benzene until a constant melting product was obtained, the substance was analyzed.

0.1705 gram substance gave 0.0931 gram CO_2, and 0.0156 gram H_2O.

0.2164 gram substance gave 23.0 cc. N at 743.6 mm. and 19°.

0.1656 gram substance gave 0.2558 gram AgBr.

0.2018 gram substance gave 0.3135 gram AgBr.

	Calculated for $Br_2C_3H_2N_2O$.	Found.
C	14.87	14.89
H	0.83	1.02
N	11.57	12.00
Br	66.11	65.74; 66.11

Dibromcyanacetamide, recrystallized from benzene, melts at 120°.5 without decomposition. Heated dry to 160° it gives off a slight amount of bromine; at 210° the evolution of bromine is marked.

Dibromcyanacetamide is very soluble in cold ether and in cold alcohol; cold benzene dissolves but little, while boiling benzene dissolves it readily; chloroform, cold or boiling, dissolves it more readily than does benzene; cold or boiling ligroïn or carbon disulphide dissolves but very little.

[1] *cf.* Ann. Chem. (Liebig), **280**, 334.

With potassium cyanide in concentrated aqueous solution, a concentrated alcoholic solution of dibromcyanacetamide becomes warm and deposits a white crystalline substance and potassium bromide. With potassium iodide iodine is liberated.

Malonic Nitrile.

Perfectly dry cyanacetamide in fine powder, intimately mixed with an equal weight of phosphorus pentachloride, is introduced into a distilling flask, whose volume is about four times that of the mixture. The bulb is connected with a Brühl's apparatus, which is then exhausted; the mixture is heated with a water-bath, and the reaction begins at about 90°, hydrochloric acid being given off in great quantities. When the liquid is boiling quietly and no more gas evolution takes place, the water-bath is replaced by a metal bath and the dark brown liquid is distilled *at once*. The distillate has generally to be redistilled twice in order to free it from traces of oxychloride of phosphorus. The yield of the purified product is upwards of 70 per cent. of the theory. The above proportion corresponds to 5 molecules of amide to 2 molecules of pentachloride. Proportions which allowed the formation of phosphorus oxychloride to take place to a great extent, rarely gave over 30 per cent. of the theoretical yield.

Malonic nitrile is a pure white, ice-like solid, melting at 29°, and boiling at 219°–220° at ordinary pressures, 99° at 11 mm. and 109° at 20 mm. On standing, even in the dark, it becomes colored. A specimen of Kahlbaum's preparation which was at least two years old, had become entirely black and, on attempting to distil it at ordinary pressure, it decomposed with great violence, emitting white fumes having the odor of ammonia and of prussic acid. In its freshly prepared aqueous solution malonic nitrile has a neutral reaction; on standing for a day it becomes quite colored, and in two weeks has become brownish and acid in reaction. Malonic nitrile has an odor faintly resembling acetamide.

0.0699 gram substance gave 26.7 cc. N at 21° and 741.6 mm.

0.1403 gram substance gave 0.0393 gram H_2O, and 0.2774 gram CO_2.

	Calculated for $C_3H_3N_3$.	Found.
C	54.54	53.92
H	3.03	3.11
N	42.42	42.61

In the combustion, malonic nitrile forms a very hard charcoal, which is burned with great difficulty. This probably explains the low result for carbon.

In the cold the malonic nitrile is soluble in about 7.5 parts of water, 2.5 parts of alcohol, 5 parts of ether, 10 parts of glacial acetic acid, 10 parts of chloroform and 15 parts of benzene. It requires more than 150 parts of cold ligroïn (boiling-point 70°–80°) for solution. It can be extracted from its aqueous solutions by ether, and these ethereal solutions must be dried with sodium sulphate, as the small amount of caustic lime in the fused calcium chloride is sufficient to turn the nitrile yellow. Sodium hydrate solution extracts malonic nitrile from ether.

Malonic nitrile dissolved in the smallest quantity of water at 20° and poured into a 30-per cent. solution of sodium hydrate ($2\frac{1}{4}$ molecules) also at 20°, and this mixture at once poured into the calculated amount of 25-per cent. sulphuric acid cooled with ice, and then extracted with ether, all the malonic nitrile is recovered. The recovered substance is tinged a very slight brown, but is not contaminated enough to materially affect the melting-point, which is found to be 28°–29°.

An excess of cold concentrated caustic soda after a long time converts malonic nitrile into malonic acid and much colored amorphous substance.

An ethereal solution of malonic nitrile shaken up with a concentrated aqueous solution of sodium carbonate for a long time, turns brown and deposits a brown amorphous flaky substance. The aqueous solution does not yield malonic nitrile on acidifying; on boiling ammonia is evolved.

Malonic Nitrile and Bromine.

The action of bromine on malonic nitrile, either molten or in aqueous solution, is complex, as oils and crystalline and amorphous solids are produced. Satisfactory observations

with regard to the nature of the oils and the amorphous bodies could not be made because of the difficulties in the way of isolating homogeneous products. In the following only the crystalline bodies, which form from 20 to 25 per cent. of the reaction-products, will be described.

Monobrommalonic Nitrile, $\begin{matrix} H \\ Br \end{matrix}\!>\!C(CN)_2$. — Ten grams of malonic nitrile dissolved in as small a quantity of water as possible, were treated with 24.8 grams (2 atoms) of bromine. The temperature of the solution rose at once, but was controlled by the tap water. After reaction had apparently ceased, the product was warmed on the water-bath until nearly all color of bromine had disappeared. The product is an oil heavier than and insoluble in water. The oil was extracted by ether and dried with sodium sulphate. On distilling off the ether a reddish brown oil remains, which when scratched becomes a magma of white crystals and red oil. The crystals were removed from the mixture and recrystallized from chloroform until a constant melting product was obtained. The yield of pure substance is small, about five grams or 25 per cent. of the theoretical.

On analysis:

0.2613 gram substance gave 45.6 cc. N at 22°.5 and 741.5 mm.

0.2182 gram substance gave 0.1981 gram CO_2, and 0.0188 gram H_2O.

0.1817 gram substance gave 0.2362 gram AgBr.

	Calculated for C_3HBrN_2.	Found.
C	24.82	24.75
H	0.69	0.91
N	19.31	19.33
Br	55.17	55.32

Monobrommalonic nitrile is a white crystalline solid melting between 65° and 66°. It is not very soluble in water or ligroïn, but is quite soluble in alcohol, ether, benzene, chloroform or carbon disulphide.

To 5 grams of monobrommalonic nitrile dissolved in 85 cc. of absolute ether were added 5.5 grams (slightly more than

one molecule) of silver nitrite, and the whole boiled for eight hours. At the end of this time the contents of the flask had a strong odor of nitrous fumes. After separation of the solid material from the ether, the latter was distilled off and the residue gave 0.8 gram of white crystalline substance melting at 118°–119°. The melting-point could not be raised by repeated crystallization. On analysis it was shown to be nearly all dibromcyanacetamide. The desired nitro-malonic nitrile had evidently not been formed.

An aqueous solution of monobrommalonic nitrile reacts at once with lead oxide, turning red and depositing lead bromide. If lead oxide be present in slight excess metallic lead is formed.

It also reacts with alkalies, lime and a silver cyanide giving off a sharp odor resembling cyanogen bromide, and amorphous red and yellow products are formed.

Dibrommalonic Nitrile, $Br_2C(CN)_2$, is prepared in a manner similar to that of the monobrom derivative. It is accompanied by much more oil and amorphous matter than is monobrommalonic nitrile, and consequently the yield is smaller. The product of the reaction is likewise an oil which is separated from the water; the water solution is extracted with ether, the ethereal solution and the oil are mixed, washed with a little water, dried with sodium sulphate and the ether distilled off. At this point a small quantity of crystals melting at 109° were obtained; the remaining oil on standing *in vacuo* over paraffin for some days partially solidified. After separating the crystals from the adhering reddish oil,[1] they were washed with much cold chloroform and finally recrystallized from boiling chloroform until the melting-point remained constant. The yield from 10 grams of nitrile is 6.5 grams, or about 17 per cent. of the theoretical.

The white crystals melting at 123°.5 to 124°, gave on analysis the following results:

0.2444 gram substance gave 0.1424 gram CO_2, and 0.0123 gram H_2O.

[1] The oil could not be made to yield any homogeneous oils or solids. It readily lost bromine on heating, liberated iodine from potassium iodide, distilled *in vacuo* with decomposition, giving a small quantity of white plates; cold or boiling alkalies did not produce cyanide, but merely gave off a sharp odor resembling that of cyanogen bromide.

0.1436 gram substance gave 16.3 cc. N at 18°.5 and 742.4 mm.

0.1165 gram substance gave 0.1951 gram AgBr.

	Calculated for $C_3N_2Br_2$.	Found.
C	16.07	15.88
H	0.00	0.56
N	12.50	12.85
Br	71.43	71.27

Dibrommalonic nitrile is quite easily soluble in alcohol, ether and boiling chloroform, and not very soluble in benzene or in ligroïn.

Silver Salt of Malonic Nitrile.—This silver salt was prepared by L. Henry[1] from ammoniacal silver-nitrate solution and malonic nitrile. He published no analytical data, but says that the amount of silver contained in it approaches that required by the formula $C_3Ag_2N_2$. This salt was prepared by pouring a cold aqueous solution of malonic nitrile (one molecule) into a cold solution of ammoniacal silver nitrate (2 molecules). The resulting white precipitate is agitated violently and set aside in a dark place for ten minutes. The salt is then filtered by means of a Hirsch funnel, washed with water until free from nitric acid, spread on clay plates and dried at 100° to 110° for several hours.

Silver determinations were made in two separate preparations and the carbon and hydrogen in a third.

0.1091 gram substance gave 0.1043 gram AgCl.

0.1326 gram substance gave 0.1293 gram AgCl.

0.6719 gram substance gave 0.3596 gram CO_2, and 0.0145 gram H_2O.

0.6999 gram substance gave 0.3790 gram CO_2, and 0.0170 gram H_2O.

0.4732 gram substance lost 0.0017 gram when heated to 110°–115° for three hours, and for three hours more to 130°–135°.

		Found.		
C	14.59	14.76		
H	0.24	0.27		
Ag			72.13	73.47

Moisture 0.36 per cent.

[1] L. Henry: Compt. Rend., **102**, 1394.

The salt is evidently a mixture of mono- and disilver malonic nitrile, for which the calculated percentages are:

	C_3HAgN_2.	$C_3Ag_2N_2$.
C	20.86	12.85
H	0.56	0.00
Ag	62.42	77.14

The analysis corresponds roughly to a mixture of about 25 per cent. of the monosilver salt, and 75 per cent. of the disilver salt; the presence of water either as such or as water of constitution is also excluded. The presence of disilver salt is shown by the behavior of the salt towards alkyl iodides.

The precipitate obtained as above described is at first white, but rapidly changes to yellow, and, after drying on a clay plate, is yellowish brown. It is soluble in an excess of ammonia from which dilute nitric acid reprecipitates it; an excess of the precipitant redissolves the salt. Heated dry to 210° it explodes with a flash of light and a slight noise, an odor resembling that of cyanogen being given off.

Silver Malonic Nitrile and Alkyl Iodides.

Diethyl Malonic Nitrile, $(C_2H_5)_2C(CN)_2$.—Silver malonic nitrile, when acted upon by ethyl iodide, pure or diluted with ether, gives diethylmalonic nitrile, ethyl isocyanide, and amorphous substances.

To 56 grams of ethyl iodide, cooled in ice, were carefully added 25 grams of silver malonic nitrile in 5 gram portions. Slight reaction takes place in the cold, the odor of isocyanide being very noticeable. This mixture is allowed to stand at the temperature of the room for seven hours, and is then heated on a bath of boiling water for twenty-one hours longer. The reaction-product was distilled with steam, the distillate extracted with ether, and the ether dried with calcium chloride; the light-brown residual oil, 4.5 grams, has an odor of isocyanide. Distillation *in vacuo* gave a liquid boiling at 91°–93° at 24 mm., which solidified on standing; after recrystallizing many times from water, 1.7 grams of a pure product (melting-point 44°) were obtained.

0.1203 gram substance gave 0.3004 gram CO_2 and 0.0926 gram H_2O.

0.0867 gram substance gave 18.0 cc. N at 22° and 747 mm.

	Calculated for $C_7H_{10}N_2$.	Found.
C	68.85	68.10
H	8.19	8.55
N	22.95	23.23

The yield of diethylmalonic nitrile is 15.6 per cent. of the theoretical.

Thirty-two grams of silver salt and 2.5 molecules of ethyl iodide, diluted with 3 volumes of absolute ether, were heated in a sealed tube at 100° for five hours, and the residue extracted with absolute ether gave finally 0.9 grams of diethylmalonic nitrile, melting at 45°, or 6.4 per cent. of the theoretical yield. The ether which was distilled off was shaken with concentrated hydrochloric acid until all odor of isonitrile disappeared; the acid solution was evaporated on the water-bath. The white deliquescent crystalline residue melted at 78° while ethylammonium chloride melts at 80° and is also deliquescent. This substance, whose weight was 0.4 gram, was therefore regarded as ethylammonium chloride. The yield is 4.3 per cent. of the total amount possible.

Besides these substances there was also formed a large amount of a reddish amorphous organic substance, probably polymerized ethyl isocyanide, which is insoluble in ether and was not further examined.

That the substance melting at 44° is diethylmalonic nitrile is shown by its conversion into diethylcyanacetamide by boiling with sodium ethylate in absolute alcohol solution, and the conversion of the latter into diethylcyanacetic and diethylacetic acids. These experiments will be described more fully further on.

Diethylmalonic nitrile is a white crystalline substance soluble in alcohol, ether, benzene, ligroïn, chloroform, acetone, and acetic ether; it is not soluble in cold water but dissolves in a small quantity of hot water, from which it crystallizes on cooling. Its aqueous and alcoholic solutions are neutral to litmus paper. It melts at 44° and is volatile with steam; boiled with alcoholic potash no ammonia or cyanide is formed.

One-half gram of the substance boiled with 15 cc. of care-

fully prepared absolute alcohol, containing two-tenths gram sodium, for twenty minutes, cooled and poured into water, extracted with ether, gave 0.45 gram of diethylcyanacetamide, which will be described later on.

One gram of diethylmalonic nitrile dissolved in 60 cc. of absolute alcohol containing 0.25 gram sodium, and allowed to stand at the temperature of the room for two hours, poured into water and extracted with ether, gave 1.1 grams of a yellow oil having a mint-like odor, and in other respects fully resembling the oil obtained by the action of ethyl iodide upon malonic nitrile and sodium ethylate in alcoholic solution. This oil will be shown later to consist of diethylmalonic nitrile and its alcohol addition-product, diethylcyanacetimidoethyl ether. This formation of imido ether from nitrile and alcohol in the presence of sodium ethylate demonstrates the additive power of the nitrile group in this compound toward alcohol and furnishes another instance of the formation of free imido ethers directly from the nitriles,[1] of which the substances described by Schmidtmann[2] are also very striking examples. The oil prepared in this way, after some time, acquired a slight odor of isonitrile, which disappeared if the flask remained uncorked for some time.

Dimethylmalonic nitrile, $(CH_3)_2C(CN)_2$.—To 70 grams of methyl iodide, cooled to —10°, were added 25 grams of silver malonic nitrile in 5-gram portions. The odor of isocyanide was soon detected and on gradually warming up to 35° the reaction became very violent. After the violence of the reaction had subsided the mixture was heated to 50° for six hours to insure completion of the reaction. The mass was now distilled with steam, the distillate extracted with ether, the ether dried, and distilled off.

The oily residue distilled at 62°–66° at 22 mm. and yielded 2.5 grams of a crystalline distillate. These crystals, after several crystallizations from ligroïn, melted at 32°.

0.1233 gram substance gave 0.0713 gram H_2O and 0.2882 gram CO_2.

[1] Nef (1895): Ann. Chem. (Liebig), **287**, 280, 322.

[2] Schmidtmann (1896): Ber. d. chem. Ges., **29**, 1193, 1174. Although Schmidtmann does not say so, yet there can be no doubt that these bodies are imido ethers.

0.1211 gram substance gave 32.9 cc. N at 22° and 737.8 mm.

	Calculated for $C_5H_6N_2$.	Found.
C	63.83	63.74
H	6.38	6.42
N	29.79	30.01

Further evidence that this substance is dimethylmalonic nitrile was obtained by converting it into dimethylmalonic acid by heating in sealed tubes with concentrated hydrochloric acid at 100° for two hours.

Dimethylmalonic nitrile is a white crystalline substance melting at 32°–32°.5, quite easily soluble in alcohol, ether, acetone, and acetic ether, not so easily soluble in chloroform, benzene, and ligroïn, and quite insoluble in water. Its alcoholic solution is neutral to litmus. Boiling with caustic soda produces no ammonia.

The formation of dialkylmalonic nitriles and of alkyl isocyanide suggests two points of attack in the silver malonic nitrile molecule, or that the compound partially decomposes into silver cyanide, and the latter reacting with the alkyl iodide produces the isonitrile. If the latter were true then there would be positive evidence as to the position of the metal in the substance since in silver cyanide the metal is bound to nitrogen.[1] This is hardly probable, since the formation of isonitrile takes place at 20°.

On the first assumption we may have two possibilities; namely, that the metal is bound to carbon or to nitrogen. The first of these is rendered unlikely because, in order to explain the formation of isonitrile, addition of alkyl iodide to the nitrile group would have to be supposed, a supposition for which there is no foundation in fact. On the second supposition the constitution to be assigned to the disilver salt would be

$$AgN : C : C : C : NAg.$$

A substance with so many consecutive double linkings would of necessity be a very reactive body.

By the addition of alkyl iodide to the double bonds between the carbon atoms the intermediate product

[1] Nef (1895): Ann. Chem. (Liebig), **287**, 269 et seq.

$$\begin{array}{ccccc} AgN : C & \cdot & C & \cdot & C : NAg \\ | & & || & & | \\ I & & R_2 & & I \end{array}$$

would be formed which, by loss of silver iodide, would give dialkylmalonic nitrile. The formation of isocyanide would be explained by the direct replacement of the silver by alkyl or by addition of alkyl iodide to the double bonds between nitrogen and carbon with subsequent loss of silver iodide. In either case, of which the first is the more likely, the compounds

$$RN : C : C : C : NR \quad \text{or} \quad AgN : C : C : C : NR$$

would be formed which could decompose with the formation of isonitrile. The isonitrile at that temperature and in the nascent state would undergo polymerization to a great extent.[1]

It is well known that silver salts react more readily by direct replacement than do the sodium salts. Consequently, the sodium derivatives of malonic nitrile with alkyl iodide should form little or no isonitrile. As a matter of fact no isocyanide is found.

These facts render the constitution given for disilver malonic nitrile very probable.

Malonic Nitrile and Sodium.

Although Schmidtmann[2] has succeeded in isolating the pure monosodium malonic nitrile, the following attempts to prepare the disodium compound will not be without interest:

To 11.5 grams of malonic nitrile dissolved in 200 cc. of absolute ether were added 8.0 grams (2 atoms) of sodium; if the nitrile is perfectly pure and dry *no reaction* of any consequence takes place. On adding a few drops of alcohol a reaction is set up at once and continues for a long time, during which a yellowish-white heavy salt, mixed with a white and lighter substance is deposited. Whenever the evolution of gas slackens a few drops more of alcohol are added to increase the action. In all, 10 cc. of alcohol were added, an amount corresponding very nearly to 1 molecule. The salt was filtered off, washed with ether, and dried. Its weight was

[1] Nef (1895): Ann. Chem. (Liebig), **287**, 357.
[2] Schmidtmann (1896): Ber. d. chem. Ges., **29**, 1171

27.13 grams. The ether filtrate contained less than 0.75 gram of dissolved material; hydrochloric acid precipitated nothing but sodium chloride and the filtrate from this contained a very small quantity of a brownish oil with a very penetrating odor. The total weight of the material taken is 27.5 grams and 27.13 grams of salt were obtained, so that very little, if any, of the nitrile escaped conversion into the salt.

Cyanides were not present in the salt.

Sodium determinations were made in two different preparations of this substance.

I. 0.5864 gram substance gave 0.4951 gram Na_2SO_4 = 27.38 per cent. Na.

II. 0.5432 gram substance gave 0.4712 gram Na_2SO_4 = 28.13 per cent. Na.

C_3HNaN_2	requires	26.13	per cent.	Na.
C_3Na_2N	"	41.82	" "	Na.
$NaOC_2H_5$	"	33.82	" "	Na.

The analysis as well as the appearance of the product make it likely that it is a mixture of at least two substances. At any rate, it reacts with alkyl iodides as though it contained both mono- and disodium malonic nitriles. A mixture of monosodium malonic nitrile and sodium ethylate in equivalent molecular proportions—the most probable composition of the product—could react as disodium malonic nitrile. Such a mixture contains 29.4 per cent. sodium, an amount not very different from that actually found.

The product obtained is a light yellow powder turning red on exposure to moist air. It dissolves readily in water, giving a yellow solution; it is slowly, but completely, soluble in alcohol. Its aqueous solution gives with silver nitrate at first a black precipitate, due probably to an excess of sodium ethylate. After removing the black precipitate, a white one is obtained on further addition of the reagent, having the same characteristics as described for the salt obtained from malonic nitrile and ammoniacal silver nitrate.

Decomposed by acids, the odor of prussic acid is obtained, and a brownish oil containing malonic nitrile melting at 27°–29° can be extracted by ether; with dilute sulphuric acid the

oil separates out at once, but with hydrochloric acid there is no separation of oil. Heated in dry condition the salt gives off ammonia and the charred residue contains cyanide and traces of carbonate. This formation of prussic acid by dilute acids is in favor of the view that the metal is bound to nitrogen, the regeneration of malonic nitrile not being a serious objection to this view, since it is not impossible that at the moment of liberation from its sodium salt malonic nitrile is

$$HN : C : C - \overset{H}{C} \equiv N,$$

of which the greater part rearranges to $CH_2(CN)_2$, while a small part escapes such rearrangement and decomposes, giving prussic acid as one of the decomposition-products.

The formation of cyanide by heating the dry, salt while not conclusive evidence, is at least of value as indirect evidence, since in cyanides the metal is bound to nitrogen.[1]

Sodium Malonic Nitrile and Ethyl Iodide.—Ten grams of the above mentioned salt were heated in a sealed tube with four molecules of ethyl iodide at 100° for eight hours. On opening the tube not a trace of isocyanide odor could be detected; prussic acid was present in the tube, as was shown by its odor, as well as by drawing air through the tube and then through caustic soda solution and showing the presence of the cyanide in the latter. The liquid contents of the tube were taken out and mixed with ether as long as any precipitate formed, which was then filtered out; the solid part of the contents of the tube was dissolved in water as far as possible, and the solution extracted with ether. The two ethereal solutions were mixed and dried with sodium sulphate. After distilling off the ether there remained an oil which on distilling *in vacuo* gave an oil boiling from 85° to 120° at 14 mm. and a solid which was identified as diethylcyanacetamide. The oily distillate was dissolved in ether, shaken out with sodium hydrate solution to remove any monoalkylated nitrile. The sodium hydrate solution after washing with ether, was poured into dilute sulphuric acid. The ether extract of this acid solution was only a very small quantity of an oil with a sharp odor. The ethereal solution which had been washed

[1] Nef (1895) : Ann. Chem. (Liebig), **287**, 269.

with alkali, was washed with water, dried and distilled. The distillate boiled at 87°–88° at 13 mm. and solidified in a freezing-mixture. After several recrystallizations from water it melted at 44° and possessed all the properties of diethylmalonic nitrile.

The yield was 2.5 grams, or 31.9 per cent. of the theoretical. The presence of prussic acid is probably due to the decomposition of monoethylmalonic nitrile.[1]

Sodium Malonic Nitrile and Methyl Iodide.—Eleven grams of sodium malonic nitrile and 57 grams of methyl iodide (four molecules) were heated in a sealed tube to 100° for 8 hours. The contents of the tube did not have any odor of isocyanide, but contained much prussic acid, which was verified in the same way as in the preceding experiment. The contents of the tube were treated in the same way as before with the additional operation of removing iodine from the ether by aqueous sodium thiosulphate. After drying and distilling *in vacuo*, an oil boiling from 50° to 70° at 11 mm., and a small quantity of a solid crystalline body were obtained. The oil was dissolved in ether and washed with sodium hydrate solution as before. Again on acidifying this alkaline solution and extracting with ether a small quantity of an oil with a sharp odor was obtained. The ethereal solution which had been washed with alkali, after distilling off the ether as before, left an oil which was almost colorless and solidified when placed on ice. After several recrystallizations from ligroïn it melted constantly at 32°–32°.5. It is dimethylmalonic nitrile, and the yield is 36 per cent. of the theory.

The solid crystalline body obtained during the distillation *in vacuo* was very small in quantity; it was found to be made up of two parts, one soluble in ether, and the other insoluble. Nothing was done with it because of the very small quantity formed.

THE ACTION OF CHLORFORMIC ESTERS AND OF ALKYL IODIDES UPON AN ALCOHOLIC SOLUTION OF MALONIC NITRILE AND SODIUM ALCOHOLATE.

a. The Action of Chlorformic Ethyl Ester.

Sodium Dicyanacetic Acid Ethyl Ester.—Five grams of

[1] P. Henry: Jahresbericht (Fittica), 1889, 639.

malonic nitrile dissolved in a small quantity of absolute ethyl alcohol were poured into 175 cc. of alcohol cooled to —15° and containing 1.75 grams (one atom) of sodium. To this mixture were added 8.5 grams (one molecule) of ethyl chlorformate. The temperature rose to +5°, and the liquid became turbid at once; the contents of the flask were cooled to —10° as rapidly as possible and then allowed to rise slowly to +10°. The liquid was neutral to litmus paper, although the odor of ethyl chlorformate was still noticeable. After vigorous agitation of the liquid the separated salt was filtered off and identified as sodium chloride; its weight was 1.9 grams or 90 per cent. of the theoretical yield. The alcohol was distilled off from the filtrate at 30–40° and 35 mm. pressure. The distillate was slightly acid and became turbid with silver nitrate. The residue was extracted with ether to remove the unchanged malonic nitrile. This ethereal extract contains, besides malonic nitrile, a substance which gives a yellowish precipitate directly with silver nitrate, and this precipitate when dried and heated on platinum foil leaves behind a fluffy, bluish-black residue. The precipitate is not due to sodium dicyanacetic ether, as will be shown later on.

The slightly yellowish residue, insoluble in ether, was extracted with boiling acetic ether, which left a small amount of sodium chloride undissolved. The acetic ether was removed by distillation, and the residue, weighing 4.2 grams or 70 per cent. of the theory, was almost white. It was purified once more by solution in 7 parts of warm alcohol and precipitating by 50 parts of ether; the crystalline precipitate is filtered off, washed with fresh ether, dried on a clay plate and then placed over paraffin *in vacuo* for 36 hours.

0.1863 gram substance gave 29.5 cc. N at 748.2 mm. and 24°.5.

0.1861 gram substance gave 0.3098 gram CO_2 and 0.0607 gram H_2O.

0.3728 gram substance gave 0.1640 gram Na_2SO_4.

	Calculated for $C_6H_5N_2O_2Na$.	Found.
N	17.50	17.53
C	45.00	45.40
H	3.13	3.62
Na	14.37	14.27

Sodium dicyanacetic ether has already been isolated, having been obtained by Haller[1] from sodic cyanacetic ether and cyanogen chloride. The salt obtained as above described has all the properties of Haller's salt: it is not soluble in chloroform, ether, ligroïn or benzene; it is soluble in about 8 parts of cold acetic ether, and the solubility is not much increased by heating. Heated dry an odor resembling that of isonitrile is first observed, and finally ammonia is given off; the residue does not contain cyanide. With boiling concentrated caustic soda this salt does not evolve ammonia, only when all the water has been driven off and the residue begins to fuse is ammonia noticeable. It does not react with dilute (1.5) sulphuric acid, but with concentrated acid it reacts at once. It dissolves in boiling concentrated hydrochloric acid from which it is again deposited unchanged in thick prisms upon cooling, and no ammonium or sodium chlorides could be detected in this deposit. The behavior towards caustic soda and hydrochloric acid is sufficient evidence of the extreme stability of this compound towards hydrolyzing agents and also shows the firm linking of the metal.

Silver nitrate produces a white curdy precipitate, which when dried has only a slight yellow tint. The dry salt heated on platinum foil gives off combustible gases having the odor of ethyl isocyanide; the residué is grayish and compact.

b. The Action of Methyl Chlorformate.

Sodium Dicyanacetic Acid Methyl Ester.—Five grams of malonic nitrile dissolved in a small quantity of absolute methyl alcohol were poured into 175 cc. of methyl alcohol containing 1.75 grams (one atom) of sodium and cooled to —15°. To this mixture 7.1 grams (one molecule) of methyl chlorformate were added at once. The temperature rose to 0°, but was soon lowered to —15°. The mixture became turbid almost immediately, and in a few moments the liquid was neutral. The greater part of the alcohol was recovered by distillation at ordinary pressure. The residual liquid, which had become slightly acid in reaction, was poured into water and extracted with ether, dried with calcium chloride,

[1] Alb. Haller (1890): Compt. Rend., III, 53-55.

and the ether distilled off. The residue is a reddish-brown oil which does not distil without decomposition at ordinary pressure, but at 10 mm. and 100° colorless malonic nitrile distils over. There remains in the bulb a mass of charcoal and white crystals. The reddish-brown oil from ethereal solution, on standing a few days, deposits crystals which are apparently monoclinic tablets, melting with partial decomposition at 206°. They give a neutral solution with boiling water, from which on cooling the substance separates out. Hot or cold ether does not take up much of it; hot alcohol dissolves it readily, cold does not. Aqueous caustic soda dissolves it readily, and from this solution it is precipitated by dilute sulphuric acid. A solution of sodium carbonate does not dissolve it. Boiling hydrochloric acid dissolves it and on cooling deposits it unchanged. A boiling solution of caustic soda does not give any ammonia; when fused with caustic soda it gives off ammonia. The amount of substance formed was about 0.05 gram.

The oil obtained from this ether was mainly malonic nitrile and contained in addition a substance giving directly with silver nitrate a yellowish precipitate which, when dried and heated on a platinum foil, swelled up and left a bluish-black mass, just as the similar substance formed in the case of ethyl chlorformate. It is not due to the presence of the sodium compound whose reaction-product with silver nitrate behaves very differently, as will be shown later.

The aqueous solution after extraction with ether was evaporated *in vacuo*, the residue extracted once more with ether, and finally with boiling acetic ether, leaving sodium chloride undissolved. There were obtained 2.9 grams of the sodium compound, or 53 per cent. of the theoretical yield. This salt was purified and dried in exactly the same manner as the corresponding ethyl compound.

0.3195 gram substance gave 0.1537 gram Na_2SO_4.

0.0838 gram substance gave 14.3 cc. N at 750.6 mm. and 17°.5.

0.1189 gram substance gave 0.1784 gram CO_2 and 0.0241 gram H_2O.

	Calculated for $C_5H_3N_2O_3Na$.	Found.
C	41.09	40.91
H	2.05	2.25
N	19.18	19.57
Na	15.75	15.60

This substance has already been isolated by Haller.[1] In addition to the description thereof given by him, it may be added that the salt is precipitated from its alcoholic solution by benzene, ligroïn, chloroform and ether; it is insoluble in acetic ether. Its behavior towards acids and alkalies, both cold and boiling, is the same as that of the corresponding ethyl derivative. The silver salt, obtained by treating the aqueous solution of the sodium compound with silver nitrate, when dried is slightly yellow, and when heated on platinum foil leaves a compact grayish residue.

c. The Action of Methyl Iodide.

Ten grams (one molecule) of malonic nitrile, dissolved in a small quantity of cold methyl alcohol, were poured into 500 cc. of cold absolute methyl alcohol containing 7 grams (two atoms) of sodium. After connecting the flask with a return-condenser, 49 grams ($2\frac{1}{4}$ molecules) of methyl iodide were added. The liquid warmed up spontaneously, but was cooled with tap water. After a few moments the flask was heated to 60° on a water-bath until the alkaline reaction disappeared. Total time of the reaction was about five minutes. The alcohol was distilled off at ordinary pressure until sodium iodide began to separate out. The remaining liquid was poured into much water, extracted with ether, the ether washed with sodium hydrate and then with water to remove any unchanged malonic nitrile and any monoalkylated product, and finally dried with calcium chloride. The light-brown oil remaining after distilling off the ether was distilled *in vacuo*. The distillate came over at 74°–76° and 22 mm.; its weight was 10.6 grams. This oil has a fragrant mint-like odor, is soluble in 8 parts of water, is decomposed by boiling with water or with methyl alcohol, giving an alkaline vapor. The aqueous solution on treatment with dilute hydrochloric acid deposits an oil suggesting the presence of imido ethers.

[1] Alb. Haller (1890): Compt. Rend., III, 53–56.

On analysis :

I. 0.0788 gram substance gave 16.5 cc. N at 19°.5 and 745 mm.

II. 0.0787 gram substance gave 16.6 cc. N at 22° and 747.4 mm.

Per cent. N found, I. 23.63; II. 23.61.

Calculated for dimethylmalonic nitrile 29.79 per cent.

Calculated for $(CH_3)_2C\begin{smallmatrix}\diagup CN\\ \diagdown C\overset{\diagup NH}{\diagdown OCH_3}\end{smallmatrix}$, 22.22 per cent.

This analysis therefore indicates the presence of about 82 per cent. of imidoether.

Methyl Dimethyl Cyanacetate, $(CH_3)_2{=}C\begin{smallmatrix}\diagup CN\\ \diagdown C\overset{\diagup O}{\diagdown OCH_3}\end{smallmatrix}$.—To prove the presence of imidoether 5 grams of the oil were dissolved in 40 cc. of water, filtered, and treated with an excess of cold hydrochloric acid. The oil which separated was filtered off, dissolved in ether, and dried with calcium chloride. On distilling *in vacuo* 2.45 grams of a colorless oil boiling at 78° and 24 mm. were obtained. The aqueous filtrate was extracted with ether, the ethereal solution washed with water, dried with calcium chloride and distilled *in vacuo*, when 0.8 gram of a colorless oil boiling from 76–78° at 20 mm. was obtained.

Nitrogen determinations were made in these oils. The oil which separated from the aqueous solution gave the following results :

I. 0.1896 gram substance gave 20.5 cc. N at 30°.5 and 741 mm.

II. 0.1647 gram substance gave 18.0 cc. N at 30° and 739 mm.

The oil extracted by ether:

III. 0.2020 gram substance gave 21.0 cc. N at 27°.5 and 741 mm.

I = 11.49 per cent.
II = 11.62 per cent.
III = 11.23 per cent.

Calculated for $(CH_3)_2 : C\begin{<}{C \vdots N}{C(=O)OCH_3}$, N = 11.02 per cent.

The oil is therefore the methyl ester of dimethylcyanacetic acid. The ammonium chloride obtained by evaporation of the aqueous solution corresponded to 3.74 grams of imido ether. The amount of imido ether obtained was 86 per cent. of this.

To prove that in the oil obtained by the action of methyl iodide upon the alcoholic solution of malonic nitrile and sodium methylate, the two methyl groups are bound to the same carbon atom, a portion of this oil was converted into dimethylmalonic acid by heating with an excess of concentrated hydrochloric acid in a sealed tube to 100° for two hours. Besides ammonium chloride, methyl chloride and some carbon dioxide, large quantities of a white crystalline substance soluble in ether were formed. This last substance after repeated recrystallization from water and ether, melted with decomposition and evolution of gas at 188°. These properties, as well as the following analysis, show the substance to be dimethylmalonic acid, already described by Thorne.[1]

0.1123 gram substance gave 0.1852 gram CO_2 and 0.0696 gram H_2O.

	Calculated for $C_5H_8O_4$.	Found.
C	45.45	44.97
H	6.06	6.88

d. The Action of Ethyl Iodide.

Diethyl Cyanacetimidoethyl Ether, $(C_2H_5)_2 = C\begin{<}{CN}{C(=NH)OC_2H_5}$. —By acting upon malonic nitrile and sodium ethylate in alcoholic solution with ethyl iodide at 72°, the proportions and the operation being the same as in the preceding experiment, an oil giving indications of the presence of imido ethers and a solid which will be shown to be diethyl cyanacetamide were obtained.

On analysis of the oil

[1] Thorne (1881): J. Chem. Soc., **39**, 544.

I. 0.1708 gram substance gave 30.6 cc. N at 23°, and 742.1 mm.

II. 0.1366 gram substance gave 24.5 cc. N at 23°.5, and 748.2 mm.

Found I. = 19.81 per cent. N; II. = 19.96 per cent. N.

Calculated for $(C_2H_5)_2 : C\begin{<}{C : N \atop NH \atop C \atop OC_2H_5}$, N = 16.66 per cent.

Calculated for $(C_2H_5)_2 : C : (CN)_2$, N = 22.95 per cent.

This analysis corresponds to a mixture of about equal parts of nitrile and imidoether. Since it has been shown that diethylmalonic nitrile on standing with alcoholic sodium ethylates gives an oil similar to the above it seemed probable that the formation of imidoether could be increased by retarding the reaction, thus allowing the nitrile, which may be formed, to become converted into imidoether under the influence of the unacted upon sodium ethylate.

This was verified in a special experiment where the reaction was allowed to take place at ordinary temperatures. Six hours were required to complete the reaction. From this mixture the oil was recovered as in the preceding cases and analyzed.

0.1226 gram substance gave 19.5 cc. N at 18°, and 740.3 mm. = 17.96 per cent. N.

This analysis corresponds to a mixture of 80 per cent. of imidoether and 20 per cent. of nitrile.

The almost complete conversion of this oil into imidoether was effected as follows: Twelve and one-half grams were dissolved in 180 cc. of absolute ethyl alcohol containing 0.75 gram sodium and allowed to stand at the temperature of the room for twenty-eight hours. The oil was then recovered in the usual way. Ten grams boiling at 90°–91° at 15 mm. were obtained; on redistillation, 8.2 grams boiling at 90°–91° at 15 mm. were obtained. The residue in the flask was oily without the slightest sign of a crystalline solid, which shows the absence of any diethyl cyanacetamide.

On analysis

0.2060 gram substance gave 31.7 cc. N at 23°, and 743.2 mm.

0.1644 gram substance gave 0.3888 gram CO_2, and 0.1408 gram H_2O.

	Calculated for $C_9H_{16}N_2O$.	Found.
C	64.27	64.49
H	9.52	9.51
N	16.66	17.04

Judging from the analysis and the steadiness of the boiling-point, the oil was apparently the pure imido ether. That such was not the case was shown when the oil was converted into

Diethylcyanacetic Ethyl Ether, $(C_2H_5)_2=C\begin{smallmatrix}CN\\ \diagup\\ C=O\\ \diagdown\\ OC_2H_5\end{smallmatrix}$.—To 7.8 grams of the imido ether dissolved in 65 cc. of-33 per cent. alcohol were added 8 cc. (2 molecules) of concentrated hydrochloric acid. The temperature of the liquid rose somewhat, but was controlled by tap water. After a short time a considerable quantity of colorless oil separated out. The mixture was now poured into water, extracted with ether, the latter washed with sodium carbonate solution, and then with pure water. After drying, distillation *in vacuo* gave 4.0 grams of colorless oil (analyzed) boiling between 100° and 101° at 15 mm., and 3.0 grams boiling between 99° and 100° and 101°–102°.

On analysis

0.1182 gram substance gave 10.3 cc. N at 23°.5, and 739.2 mm.

0.1774 gram substance gave 0.4275 gram CO_2, and 0.1422 gram H_2O.

	Calculated for $C_9H_{16}NO_3$.	Found.
C	63.90	65.71
H	8.87	8.96
N	8.28	9.57

The oil is evidently the desired substance containing traces of another compound richer in carbon and nitrogen than itself, in all probability diethylmalonic nitrile. In order to test this 5.25 grams of the oil were dissolved in 90 cc. of

absolute ethyl alcohol containing 0.4 gram sodium, and the mixture allowed to stand at the temperature of the room for thirteen days. The liquid was now poured into water, treated with an excess of hydrochloric acid, and extracted with ether as before. The second distillation *in vacuo* yielded 3.1 grams of an oil boiling at 100–101° at 14 mm.

On analysis

0.1874 gram substance gave 14.4 cc. N at 21°, and 745 mm.

0.1630 gram substance gave 0.3816 gram CO_2, and 0.1293 gram H_2O.

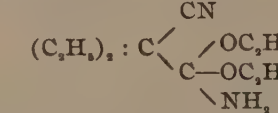
	Calculated for $C_9H_{15}NO_2$.	Found.
C	63.90	63.84
H	8.87	8.81
N	8.28	8.61

Diethylcyanacetic ether is a colorless oil with a fragrant odor, entirely different from the refreshing mint-like odor of the imido ether. It is not very soluble in water and its solubility in 33-per cent. alcohol is less than that of the imido ether.

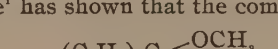
Although the diethylcyanacetimidoether described above has not been obtained in a perfectly pure state, yet it cannot be doubted that if the mixture of nitrile imido ether and alcoholic sodium ethylate had been allowed to stand longer, no unchanged nitrile would have remained. The only slightly contaminated specimen of diethylcyanacetimidoethyl ether is a colorless mobile oil possessing a fragrant and refreshing mint-like odor. It is only slightly soluble in water, and can be boiled without decomposition with water and ethyl alcohol.

Diethylcyanacetamide, $(C_2H_5)_2{=}C\begin{smallmatrix}\diagup\!\!\diagup\,CN\\ \diagdown\!\!\diagup\,C{=}O\\ \diagdown\,NH_2\end{smallmatrix}$.—This substance is formed in the preparation of diethylmalonic nitrile from the sodium salt and ethyl iodide in sealed tubes; in the action of ethyl iodide upon malonic nitrile and sodium ethylate in alcoholic solution; and when diethylmalonic nitrile is boiled with absolute alcohol containing 1.3 per cent. of sodium.

In this last method the alcohol had been made absolute with the greatest of care and it is not reasonable to suppose that the formation of amide is caused by the presence of water or of sodium hydrate. This is probably due to the intermediate production of the dialkylamidoether,



which at the boiling-point of alcohol must lose ethyl ether and form the amide. Such a loss of ether is not improbable since Mackenzie[1] has shown that the compound



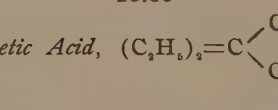
on standing over sulphuric acid in a desiccator, loses ether, and that with acid it forms benzophenone.

Diethylcyanacetamide melts at 120°, is white, and crystallizes in plates. It is soluble in alcohol, ether, and chloroform, and not very soluble in ligroïn or benzene.

0.1516 gram substance gave 0.1187 gram H_2O, and 0.3337 gram CO_2.

0.1194 gram substance gave 21.3 cc. N at 21°, and 746.9 mm.

	Calculated for $C_7H_{12}N_2O$.	Found.
C	60.00	60.02
H	8.57	8.69
N	20.00	20.05

Diethylcyanacetic Acid,  .—This substance has been made (1) from the oil obtained by the action of ethyl iodide upon malonic nitrile and sodium ethylate in alcoholic solution, (2) from diethylmalonic nitrile and (3) from diethylcyanacetamide by heating in sealed tubes with concentrated hydrochloric acid to 100° for two hours. In all cases a brownish oil floats on top of the hydrochloric acid in the tube. The oil is separated, the acid solution is mixed with

[1] (1896) Chem. News, **73**, 268.

enough water to dissolve the ammonium chloride, and shaken out with ether. The ethereal solution and the separated oil are mixed and shaken out with a solution of sodium carbonate. This carbonate solution, after being washed with fresh ether, is acidified, and again shaken out with ether; the ether washed with water, dried, and distilled. There is obtained a colorless oil boiling between 162° and 164°, at 18 mm. The oil soon solidifies to a white, hygroscopic, ice-like solid. It melts at 57° and distils undecomposed at ordinary pressure, a rather striking property of a cyanogen acid. The cyanogen group is very stable, not being affected by concentrated hydrochloric acid in a sealed tube at 120° for one hour, nor by heating with alcoholic potash in a sealed tube to 100° for three hours. A silver salt is obtained when sodium hydrate is added to a mixture of the acid and silver nitrate. The salt crystallizes from boiling water in glistening needles, which are not affected by light.

0.1847 gram substance (free acid) gave 0.1302 gram H_2O, and 0.4012 gram CO_2.

0.2534 gram substance gave 22.5 cc. N at 18°, and 749 mm.

	Calculated for $C_7H_{11}NO_2$.	Found.
C	59.57	59.23
H	7.80	7.83
N	9.93	10.15

By heating with concentrated hydrochloric acid in a sealed tube to 160° for eight hours diethylcyanacetic acid is quantitatively converted into

Diethylacetic Acid.—This acid was isolated in the same way as the preceding acid, except that it was distilled at ordinary pressure, boiling from 189–191°.[1] The portion coming over between 189°.5 and 190°.5 was analyzed.

0.1766 gram substance gave 0.1624 gram H_2O, and 0.3998 gram CO_2.

	Calculated for $C_6H_{12}O_2$.	Found.
C	62.07	61.73
H	10.35	10.22

The acid also forms the peculiar silver salt so characteristic of diethylacetic acid.[2]

[1] Saytzeff (1878): Ann. Chem. (Liebig), **193**, 351. [2] *Ibid.* p. 353.

The conversion of diethylcyanacetic acid into diethylacetic acid furnishes the proof that in all those substances yielding diethylcyanacetic acid the two ethyl groups are bound to one and the same carbon atom.

In the foregoing reasons have been given for considering that the metal in metallic derivatives of malonic nitrile is bound to nitrogen. On this basis the alcoholic solution of malonic nitrile and sodium alcoholate must be regarded as containing monosodic malonic nitrile,[1] CN—CH=C=NNa. The alkyl iodide, adding itself to the double bond between the two carbon atoms, produces, with loss of sodic iodide, monoalkylated malonic nitrile, CN—CHR—CN, which, in the presence of the excess of sodium ethylate, must immediately be converted into the sodium salt, CN—CR=C=NNa; the latter then gives, by absorption of alkyl iodide,

$$\begin{array}{l} \mathrm{CN{-}CR{-}C{=}NNa}\ (A). \\ \quad\ |\quad\ | \\ \quad\ \mathrm{R}\quad \mathrm{I} \end{array}$$

The product (*A*) by loss of sodic iodide, yields dialkylmalonic nitrile. The formation of the monimido ether,

$$\begin{array}{l} \mathrm{CN{-}CR_2{-}C:NH}, \\ \qquad\quad\ | \\ \qquad\quad \mathrm{OR} \end{array}$$

which, as has been seen, is, in the case of methyl—as well as of ethyl iodide, the chief product of the reaction, can be explained (1) on the assumption that the above intermediary product (*A*) reacts directly, as an acid iodide,[2] with the alcohol present, *i. e.*, before loss of sodic iodide takes place, or (2) on the assumption that the dialkylmalonic nitrile first formed in the reaction subsequently adds, in part, one molecule of methyl or of ethyl alcohol in view of the presence of sodium alcoholate. Since it has been shown that diethylmalonic

[1] There are no facts as yet known which in any way prove that a disodium salt of malonic nitrile or of malonic ether exists, and, on the whole, the existence of such salts seems at present improbable. We know with certainty that with an excess of sodium ethylate, cyanamide gives only the monosodium salt, NaHN—CN, notwithstanding that this compound readily gives a disilver salt, Ag_2N—CN.

The action of alkalies, mild and caustic, on malonic nitrile, as well as a careful study of the behavior of the salts of malonic nitrile and of monoalkylated malonic nitriles towards acids, acyl and alkyl chlorides, will be continued in this laboratory. J. U. Nef.

[2] *Cf.* Nef (1895): Ann. Chem. (Liebig), **287**, 263, 315, 317–18, 343.

nitrile does actually, although very slowly, absorb ethyl alcohol with formation of the monimidoether in case some sodium ethylate is at hand, it is manifestly impossible, with the experimental data as yet available, to come to a decision as to the actual course of the generation of the monimidoether.

The formation of imido ethers, however, under the circumstances just mentioned, makes it necessary to take the possibility of their presence into consideration in all cases where the Conrad-Limpach method is applied to substances containing nitrile groups.